




Toward better magnetic materials

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Group News Slides





Outline

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 - Isotropic Interaction
 - Zero-field Splitting
 - # Computational Details
 - # Results
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 - Singlet-Triplet splitting and Isotropic Interaction
 - Special Case of $\text{Ti}_2\text{F}_2\text{H}_4$
 - Spin-Orbit Coupling calculations and timings
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 - # Summary
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Background

- # Bonding and magnetic properties of materials involve complex interactions between metal centers and ligands
- # It is important to understand how changes in ligands affect the magnetic properties of a system.
- # Copper(II) compounds (d^9) have been extensively studied in the past
- # Like the copper(II) compounds, titanium(III) compounds (d^1) have one unpaired electron on each metal center, but differ from copper in orbital occupation and size
- # Numerous titanium compounds have interesting magnetic properties

Background (cont.)

- # Many experimentally known dititanium(III) molecules have a planar ring structure (see next slide)
- # The D_{2h} isomers of $Y_2Ti_2(\mu-X)_2Y_2$ are models for these compounds
- # Ti_2H_6 has been studied previously*
- # We wish to understand trends in magnetic properties as X and Y are replaced by the halogens F, Cl, Br

* S. P. Webb, M. S. Gordon, *J. Am. Chem. Soc.* **120**, 3846 (1998).
S. P. Webb, M. S. Gordon, *J. Chem. Phys.* **109**, 919 (1998).

R. Jungst, D. Sekutowski, J. Davis, M. Luly, and G. Stucky, *Inorg. Chem.*, **1977**, 16, 1645.

Magnetic Properties

- # A variety of factors influence magnetic properties for a dinuclear compound:
 - Isotropic interaction (singlet-triplet splitting)
 - Zeeman perturbation (due to a magnetic field)
 - Asymmetry
 - Local Anisotropy (local spin $>1/2$)
 - Dipolar interaction
 - Anisotropic (pseudodipolar) interaction
 - ❖ For the highly symmetric titanium(III) molecules, neither asymmetry or local anisotropy affects the magnetic properties

Isotropic Interaction

- ✦ Usually the dominant effect
- ✦ Formally described as coupling between local spin operators S_A and S_B .
- ✦ The Hamiltonian for the coupling may be written

$$H = -2J S_A \cdot S_B$$

- ✦ The isotropic exchange interaction parameter is defined by

$$2J = E(S=0) - E(S=1)$$

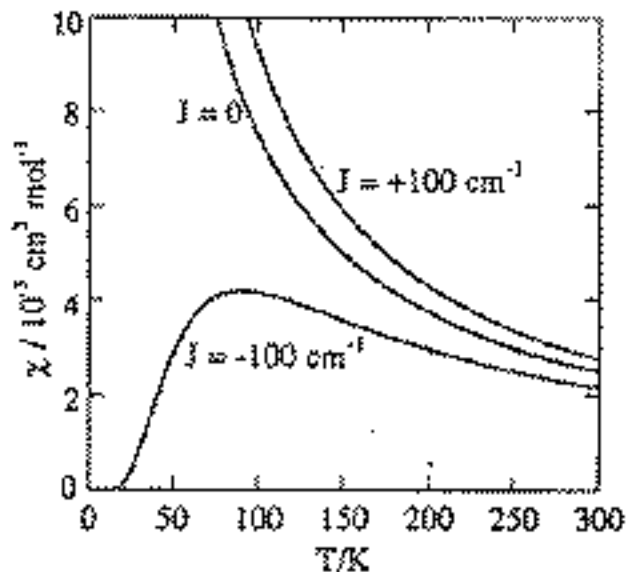
- ✦ When $J < 0$, the singlet state is the ground state and the interaction is antiferromagnetic
- ✦ When $J > 0$, the triplet state is the ground state and the interaction is ferromagnetic

Isotropic Interaction

- # When the isotropic interaction is the dominant effect, the spin quantum numbers $S=0$ and $S=1$ are good quantum numbers
- # For an antiferromagnetic compound ($J < 0$), the magnetic susceptibility goes through a maximum at the Néel temperature T_{\max} such that

$$|2J| / kT_{\max} = 1.599$$

where k is the Boltzmann constant



Zero-Field Splitting

- # Other magnetic properties can be especially important when
 - Triplet state is ground state or
 - Isotropic interaction is small
- # Zero-field splitting in an EPR spectrum is caused by the interaction of two local doublets according to

$$H = \mathbf{S} \cdot \mathbf{g} \mathbf{H} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$

where H is the magnetic field, μ_B is the Bohr magneton, \mathbf{S} is the spin operator ($\mathbf{S} = \mathbf{S}_A = \mathbf{S}_B$), \mathbf{g} is the \mathbf{g} tensor, and \mathbf{D} is the zero-field splitting tensor

Zero-Field Splitting

- ✦ The axial and rhombic zero-field splitting parameters are calculated from the principal values of \mathbf{D} by

$$D = 3D_z/2$$

$$E = (D_x - D_y)/2$$

- ✦ The dipolar term is often the minor contribution to \mathbf{D} and may be estimated from the point dipole approximation
- ✦ The pseudodipolar term is related to spin-orbit coupling
- ✦ The parameters D and E are composed of dipolar contributions D_d and E_d and pseudodipolar contributions D_e and E_e

$$D = D_d + D_e$$

$$E = E_d + E_e$$

Computational Details

- # Basis sets used:
 - TZV(p) (optimizations, SOC)
 - TZVP(f) (energies)
 - TZVP(f,g) (energies)
- # MCSCF(2,2) geometry optimizations for singlets
- # ROHF geometry optimizations for triplets
- # Hessians used to characterize stationary points
- # Dynamic electron correlation included using MRMP2 and ZAPT2 calculations at stationary points
- # All calculations done with GAMESS
- # Molecules and orbitals visualized with MacMolPlot

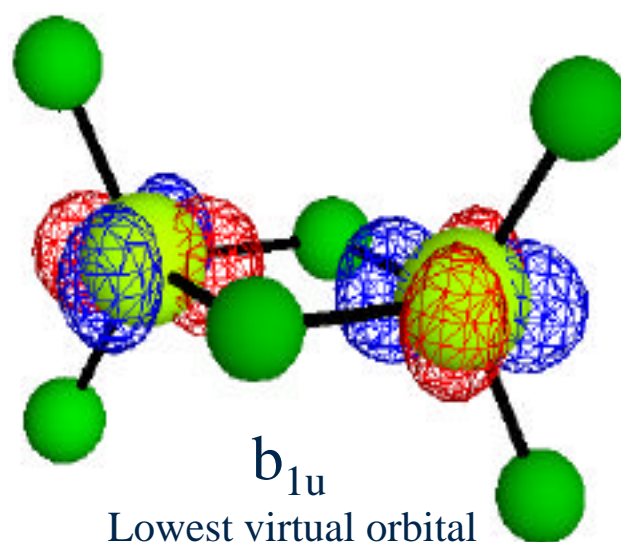
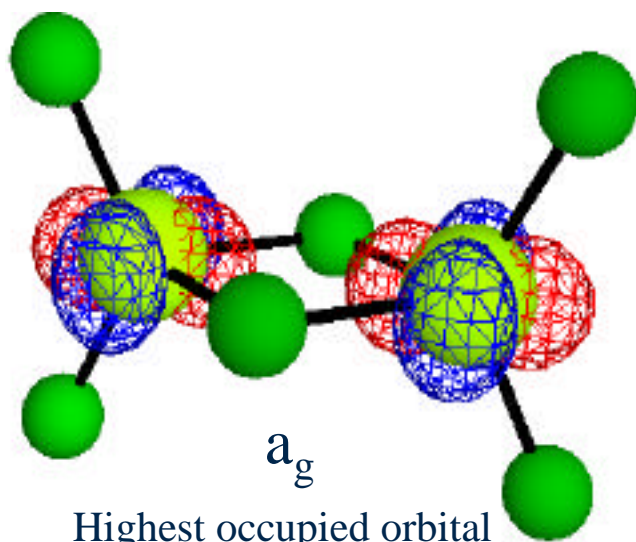
Results:

Electronic Structure

- # Mulliken populations show charges on Ti range from +0.73 to +1.78, indicating highly polarized Ti-ligand bonds
- # The lowest energy singlet and triplet states are 1A_g and $^3B_{1u}$ respectively
- # The singlet states have at least 0.87 electrons in the lowest virtual orbital (from natural orbital analysis- see next slide)
- # These states are essentially singlet diradicals
- # There is probably very little direct Ti-Ti bonding based on natural orbital occupations numbers (NOON's)

Natural Orbital Occupation Numbers

Molecule	a_g Occupation Number	b_{1u} Occupation Number
$\text{Ti}_2\text{H}_2\text{F}_4$	1.13	0.87
$\text{Ti}_2\text{H}_2\text{Cl}_4$	1.11	0.89
$\text{Ti}_2\text{H}_2\text{Br}_4$	1.10	0.90
$\text{Ti}_2\text{F}_2\text{H}_4$	1.00	1.00
$\text{Ti}_2\text{Cl}_2\text{H}_4$	1.04	0.96
$\text{Ti}_2\text{Br}_2\text{H}_4$	1.05	0.95
Ti_2F_6	1.01	0.99
Ti_2Cl_6	1.03	0.97
Ti_2Br_6	1.05	0.95



Singlet-Triplet Splitting

- # Dynamic electron correlation is required for calculating accurate energy gaps.
- # Without correlation, some triplet states lie below the singlet states (these are Ti_2F_6 , Ti_2Cl_6 , Ti_2Br_6 , and $\text{Ti}_2\text{Cl}_2\text{H}_4$). With correlation, all singlets are lowest in energy.
- # Singlet-triplet splitting increases by 0.4-1.3 kcal/mol from TZV(p) to TZVP(f) and another 0.2-0.8 kcal/mol from TZVP(f) to TZVP(f,g) as we increase the basis set size.

$E(S=1) - E(S=0)$ (kcal/mol)

Molecule	TCSCF/TZVP	MRMP/TZVP	TZVP(f)	TZVP(f,g)
$\text{Ti}_2\text{H}_2\text{F}_4$	0.83	4.64	5.30	5.48
$\text{Ti}_2\text{H}_2\text{Cl}_4$	0.59	4.83	5.67	5.84
$\text{Ti}_2\text{H}_2\text{Br}_4$	0.52	4.97	5.80	5.95
$\text{Ti}_2\text{Cl}_2\text{H}_4$	-0.04	2.90	4.13	4.24
$\text{Ti}_2\text{Br}_2\text{H}_4$	0.02	3.30	4.47	4.88
Ti_2F_6	-0.12	2.20	2.64	2.79
Ti_2Cl_6	-0.09	3.17	4.43	5.20
Ti_2Br_6	-0.02	4.04	5.22	*

* Largest calculation does not work yet

Isotropic Interaction

- # Isotropic interaction follows same trends as singlet-triplet splitting
- # These isotropic interaction parameters are much larger than experimental J values for compounds with halide bridges and organic terminal ligands (-70 cm^{-1} to -138 cm^{-1})
- # So, we need to study organic terminal ligands in the future

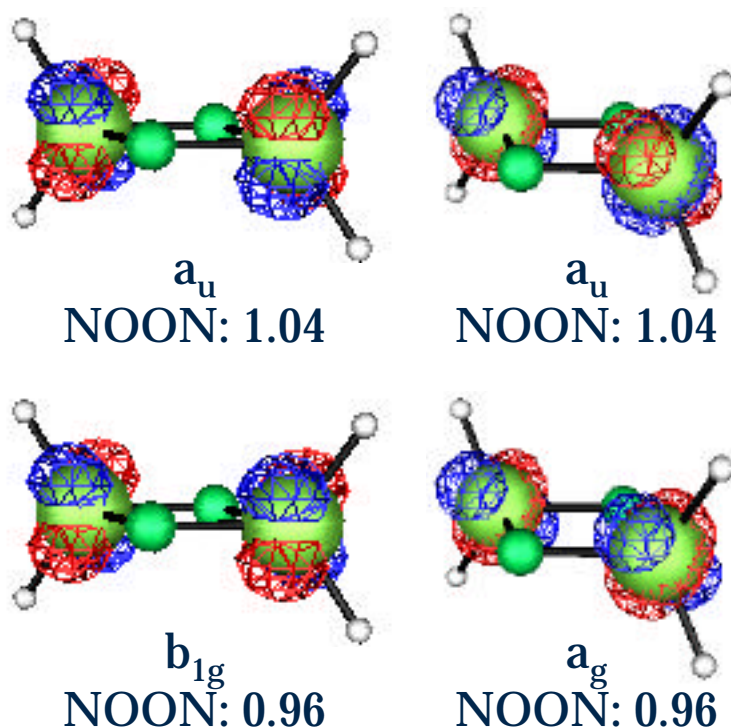
Isotropic Interaction J (cm^{-1})

Molecule	MCSCF/TZVP	MRMP/TZVP	TZVP(f)	TZVP(f,g)
$\text{Ti}_2\text{H}_2\text{F}_4$	-144	-812	-926	-958
$\text{Ti}_2\text{H}_2\text{Cl}_4$	-103	-845	-992	-1020
$\text{Ti}_2\text{H}_2\text{Br}_4$	-90	-869	-1014	-1040
$\text{Ti}_2\text{Cl}_2\text{H}_4$	7	-506	-722	-741
$\text{Ti}_2\text{Br}_2\text{H}_4$	-4	-577	-782	-853
Ti_2F_6	20	-384	-461	-487
Ti_2Cl_6	15	-554	-775	-910
Ti_2Br_6	4	-706	-913	*

* Largest calculation does not work yet

Ti₂F₂H₄ - Special Case

- # Lowest energy D_{2h} singlet is ¹A_g state
- # Lowest energy triplet is a ³B_{1u} state.
- # Two possible configurations:
 $(\sigma)^2(\sigma^*)^2$ combination versus $(\pi)^2(\pi^*)^2$ combination.
- # Neither is a minimum on the PES (by analytical GVB calculations)
- # C_{2h} singlet is the minimum energy structure.



Relative energies in kcal/mol

Structure	Singlet	
	MCSCF	MRMP2
$(\sigma)^2(\sigma^*)^2$	1.17	1.77
$(\pi)^2(\pi^*)^2$	0.30	0.46
C _{2h}	0.00	0.00
Structure	Triplet	
	ROHF	ZAPT2
$(\sigma^*)^{1,1}$	1.05	4.32
$(\pi^*)^{1,1}$	0.41	3.29
C _{2h}	0.08	2.86

Spin-Orbit Coupling

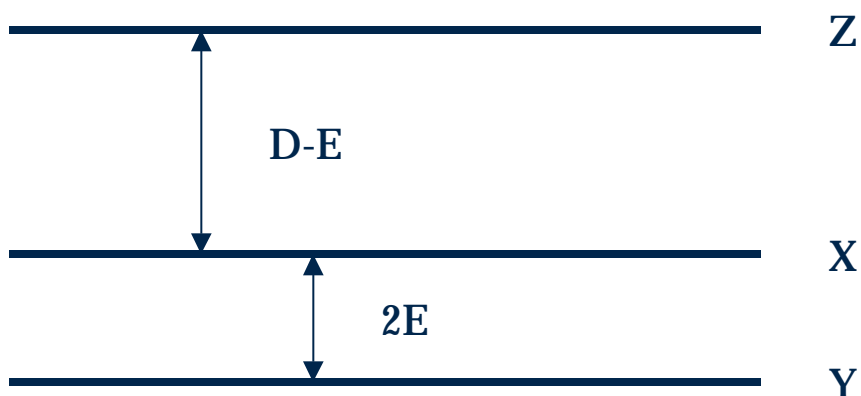
- # Used two kinds of spin-orbit coupling calculations:
 - CASSCF-SOC
 - MCQDPT-SOC
- # Used three kinds of spin-orbit coupling operators:
 - HSO1
 - HSO2P
 - HSO2
- # Twenty states used in the calculations
- # Zero field splitting (ZFS) parameters calculated using all 6 methods
- # Timings compared for the 6 methods

State Mixings

- # Eigenvectors of spin-mixed states show which adiabatic states mix with predominant state
- # Direct product of predominant state and mixing state shows angular momentum operator responsible for mixing (i.e. L_z , L_x)
- # D_e and E_e calculated from

$$D = (Z - X) + E$$

$$E = (X - Y)/2$$



SOC Results

- # Except for $\text{Ti}_2\text{F}_2\text{H}_4$, spin-orbit coupling results are very close to values for Ti_2H_6
- # D_e and E_e are in the range of experimentally observed parameters for similar Ti and Cu compounds.
- # HSO2P energies are the same as HSO2 energies to second decimal place ;
ZFS parameters are very similar for HSO1, HSO2P, and HSO2
- # As we move from CASSCF-SOC to MCQDPT-SOC, most magnitudes increase except Ti_2Cl_6 and Ti_2Br_6 magnitudes decrease slightly
- # Coefficients for mixing same as HSO2 to $\pm.00002$ for HSO2P and $\pm.002$ for HSO1

ZFS Parameters

		CASSCF-SOC			MCQDPT-SOC		
		HSO1	HSO2P	HSO2	HSO1	HSO2P	HSO2
Ti ₂ H ₂ F ₄	D _e	-0.087	-0.094	-0.099	-0.112	-0.123	-0.129
	E _e	0.086	0.091	0.093	0.106	0.118	0.118
Ti ₂ H ₂ Cl ₄	D _e	-0.086	-0.093	-0.104	-0.137	-0.157	-0.166
	E _e	0.087	0.094	0.096	0.116	0.134	0.135
Ti ₂ H ₂ Br ₄	D _e	-0.088	-0.092	-0.105	-0.137	-0.156	-0.165
	E _e	0.089	0.094	0.096	0.115	0.130	0.132
Ti ₂ F ₂ H ₄ C _{2h}	D _e	0.916	0.950	0.890	1.690	1.660	1.556
	E _e	0.038	0.044	0.045	-0.035	-0.079	-0.079
	D _e	0.521	0.548	0.508	0.220	0.257	0.230
	E _e	0.001	0.001	0.002	0.021	0.051	0.050
	D _e	0.537	0.564	0.524	0.251	0.160	0.130
	E _e	0.004	0.005	0.005	-0.118	-0.232	-0.232
Ti ₂ Cl ₂ H ₄	D _e	0.008	0.004	-0.003	0.078	0.076	0.067
	E _e	0.048	0.054	0.056	0.044	0.058	0.059
Ti ₂ Br ₂ H ₄	D _e	0.022	0.016	0.009	0.104	0.100	0.093
	E _e	0.037	0.045	0.047	0.033	0.043	0.044
Ti ₂ F ₆	D _e	0.002	0.010	0.014	-0.041	-0.036	-0.032
	E _e	0.013	0.019	0.023	-0.030	-0.021	-0.017
Ti ₂ Cl ₆	D _e	-0.026	-0.030	-0.035	-0.016	-0.020	-0.025
	E _e	0.039	0.043	0.044	0.028	0.034	0.035
Ti ₂ Br ₆	D _e	-0.016	-0.020	-0.024	-0.012	-0.016	-0.019
	E _e	0.028	0.034	0.034	0.022	0.027	0.028

CASSCF-SOC

Timings

		Total CPU Time ^a	Spin Orbit Coupling ^b	% Time Required	% Time Required
Ti ₂ H ₂ F ₄	HSO1	178	37	2.3	0.5
	HSO2P	4292	4153	56.1	55.1
	HSO2	7656	7536	100.0	100.0
Ti ₂ H ₂ Cl ₄	HSO1	270	81	1.9	0.6
	HSO2P	6053	5860	42.8	42.1
	HSO2	14141	13927	100.0	100.0
Ti ₂ H ₂ Br ₄	HSO1	861	359	2.9	1.2
	HSO2P	17408	16963	58.2	57.5
	HSO2	29914	29516	100.0	100.0
Ti ₂ Cl ₂ H ₄	HSO1	148	35	1.7	0.4
	HSO2P	3618	3505	40.5	39.8
	HSO2	8921	8807	100.0	100.0
Ti ₂ Br ₂ H ₄	HSO1	294	92	2.0	0.6
	HSO2P	6467	6266	43.7	42.9
	HSO2	14800	14598	100.0	100.0
Ti ₂ F ₆	HSO1	230	56	1.6	0.4
	HSO2P	6356	6181	43.8	43.1
	HSO2	14514	14352	100.0	100.0
Ti ₂ Cl ₆	HSO1	473	167	1.5	0.5
	HSO2P	10180	9871	32.2	31.5
	HSO2	31600	31304	100.0	100.0
Ti ₂ Br ₆	HSO1	1780	1029	2.4	1.4
	HSO2P	35267	34430	47.1	46.4
	HSO2	74895	74138	100.0	100.0

HSO2P takes ~40-50% of time required for HSO2

a. Timings for a 300 MHz uSPARC2 computer.

b. This category includes time required for integral transformations and spin-orbit matrix element calculation.

MCQDPT-SOC

Timings

		Total CPU Time ^a	Spin Orbit Coupling ^b	% Time Required	% Time Required
Ti ₂ H ₂ F ₄	HSO1	2192	58	59.4	3.8
	HSO2P	3171	1022	85.9	67.3
	HSO2	3692	1519	100.0	100.0
Ti ₂ H ₂ Cl ₄	HSO1	4472	105	68.4	4.6
	HSO2P	6022	1579	92.2	68.8
	HSO2	6534	2297	100.0	100.0
Ti ₂ H ₂ Br ₄	HSO1	18638	364	81.0	6.4
	HSO2P	20683	3366	89.9	59.2
	HSO2	22997	5682	100.0	100.0
Ti ₂ Cl ₂ H ₄	HSO1	2104	57	62.8	4.3
	HSO2P	2909	860	86.8	65.8
	HSO2	3350	1307	100.0	100.0
Ti ₂ Br ₂ H ₄	HSO1	4797	112	67.1	4.7
	HSO2P	6213	1538	86.9	64.4
	HSO2	7151	2388	100.0	100.0
Ti ₂ F ₆	HSO1	3863	90	62.6	3.7
	HSO2P	5111	1501	82.8	62.2
	HSO2	6174	2413	100.0	100.0
Ti ₂ Cl ₆	HSO1	9560	182	73.3	4.2
	HSO2P	11137	2471	85.4	56.5
	HSO2	13049	4375	100.0	100.0
Ti ₂ Br ₆	HSO1	50172	800	81.7	7.1
	HSO2P	63879	6745	104.1	59.7
	HSO2	61380	11304	100.0	100.0

HSO2P takes ~60% of time required for HSO2


a. Timings for a 200 MHz IBM Power3 computer.

b. This category includes time required for integral transformations and spin-orbit matrix element calculation.



Future Directions

Expand work to study the magnetic properties of systems with more complicated ligands.

- Replace terminal ligands with large organic ligands such as cyclopentadienyl rings
 - Modify bridging ligands to study the effects of other groups in the periodic table
(e.g. μ -OR, -SH, -NH₂, -PH₂, -NNN)
- 

Summary

- # Compounds have high degree of diradical character and very small bonding interaction
- # Dynamic electron correlation required for calculating accurate energy gaps
- # All Ti compounds studied so far are antiferromagnetic
- # Antiferromagneticity increases F Cl Br, both for bridging and terminal ligands
- # Spin-orbit coupling effects similar to those previously reported for Ti_2H_6
- # HSO1, HSO2P, and HSO2 calculate similar ZFS parameters; magnitude of MCQDPT-SOC calculations usually greater than CASSCF-SOC
- # HSO2P and HSO2 calculate energies that are virtually the same, but the former requires 30-60% less time for the spin-orbit coupling part of the calculations



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